

AD 676903

URS 678-4

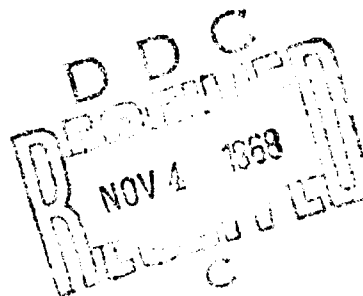
IMPROVEMENT OF THE PERFORMANCE OF CARBON  
SMOKE GENERATORS BY THE CHOICE OF  
FUELS AND FUEL ADDITIVES

Final Report

July 8, 1968

OCD Work Unit 2552C T.O. No. 2550(67)

Contract Number NOC22867C2089



URS SYSTEMS  
CORPORATION

This document has been approved for public release and  
sale; its distribution is unlimited.

NRDL-TFC-69-41

Summary  
URS 678-4

URS ■ SYSTEMS  
C O R P O R A T I O N

Summary Report  
of  
IMPROVEMENT OF THE PERFORMANCE OF CARBON  
SMOKE GENERATORS BY THE CHOICE OF  
FUELS AND FUEL-ADDITIVES

Final Report

July 8, 1968

by  
Thomas Goodale

Prepared for  
OFFICE OF CIVIL DEFENSE  
Office of the Secretary of the Army  
Washington, D.C. 20310  
through  
U.S. Naval Radiological Defense Laboratory  
San Francisco, California 94135

This report has been reviewed in the Office of Civil Defense and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Office of Civil Defense.

Each transmittal of this document outside the agencies of the U.S. Government must have prior approval of OCD Research.

The smoke yield of the fuel was measured as a function of the improvement in the performance of the engine. The smoke yield of a type considered for use in a thermal engine was measured. This could be obtained by choice of appropriate fuel and the addition of additives to the fuel. The improvement of performance of the engine was measured by the weight of fuel carbon as smoke and generation of less heat.

The smoke yield, defined as the weight of carbonaceous smoke recovered per unit weight of fuel in the fuel burned, was measured for 35 different pure hydrocarbons under closely controlled conditions in a laboratory generator. The laboratory generator was geometrically similar to one previously employed, experimentally, in the original countermeasure program.

The following general classes of additives were tested for their effect on the smoke yield of hydrocarbon fuels.

1. Acids and bases (electron acceptors and donors) and known flame inhibitors
2. Oxygen, in the form of oxygen-enrichment of the air supply
3. Selected hydrocarbons of high intrinsic smoke yield as additives to hydrocarbons of lower smoke yield
4. Compounds capable of initiating energetic reaction at moderate temperatures (triethylaluminum and cyanuric triazide)
5. Solid dehydrogenation catalysts

Findings were as follows:

1. The extreme values of smoke yield, of various pure hydrocarbons tested, differed by a factor of fifteen.

2. A tentative correlation was discovered between the smoke yields of pure hydrocarbons and their strength as carbon acids.
3. If compounds of questionable stability in long-term storage are excluded, the isomers of xylene offer the highest smoke production per unit weight of fuel of any fuel tested.
4. Strong Lewis-acids and bases were found to be active in promoting increase in smoke yield; however, the increases were modest, being of the order of 35 percent or less. Halogen-containing flame inhibitors also increased smoke yield. The effectiveness of these additives have an inverse relationship to the intrinsic smoke yield of the fuel. An argument is presented to show that this inverse relationship may be a consequence of the correlation between smoke yield and carbon acid strength mentioned in item 2, above.
5.  $\text{Fe}(\text{CO})_5$  and  $\text{CrO}_2\text{Cl}_2$ , which are reported to show the highest order of effectiveness as flame inhibitors, apparently inhibit formation of smoke.
6. When the air supply to the smoke generator was enriched in oxygen to a composition 50 percent oxygen and 50 percent nitrogen, other parameters remaining unchanged, the smoke yield of benzene was increased more than a factor of two. The smoke yields of other fuels tested in the enriched air supply increased a modest amount or showed little change.
7. A solution of 5.78 weight percent of a hydrocarbon of high smoke yield (indene) in a hydrocarbon of low smoke yield (n-decane) produced a higher smoke yield by 25 to 50 percent than would have been obtained from its components if each had been burned alone, indicating indene to be active in promoting the smoke yield of n-decane.
8. An increase in smoke yield of about 20 percent was observed for fuels burning over granular, solid catalysts having acidic surfaces (activated alumina, and phosphorous pentoxide on diatomaceous earth) and over one having a basic surface (sodium amide on diatomaceous earth) compared with the same fuels burning alone.

Recommendations are:

1. Further chemical investigation intended to improve the performance of carbon smoke generators should seek an understanding of the mechanism of formation of carbonaceous smoke.
2. In the immediate term, it is recommended that an investigation be conducted of the extent to which the performance of a full-scale prototype smoke generator, employing a hydrocarbon fuel with air as oxidizer, can be improved by optimizing the mode of mixing and degree of turbulence of the streams of fuel vapor and air, for greatest production of smoke.

URS 678-4

IMPROVEMENT OF THE PERFORMANCE OF CARBON  
SMOKE GENERATORS BY THE CHOICE OF  
FUELS AND FUEL ADDITIVES

Final Report

July 8, 1968

OCD Work Unit 2552C T.O. No. 2550(67)

Contract Number N0022867C2089

by

Thomas Goodale  
URS SYSTEMS CORPORATION  
1811 Trousdale Drive  
Burlingame, California 94010

for

OFFICE OF CIVIL DEFENSE  
Office of the Secretary of the Army  
Washington, D.C. 20310

through

U.S. Naval Radiological Defense Laboratory  
San Francisco, California 94135

This document has been approved for public release and  
sale; its distribution is unlimited.

OCD REVIEW NOTICE

This report has been reviewed in the Office of Civil Defense and  
approved for publication. Approval does not signify that the  
contents necessarily reflect the views and policies of the Office  
of Civil Defense.

## ABSTRACT

An experimental investigation was conducted of the improvement in performance of a simple carbon smoke generator, employing a hydrocarbon fuel and air as oxidizer, that could be obtained by appropriate choice of fuels and of various additives to the fuels. The smoke yield of pure hydrocarbons, defined as the weight of carbonaceous smoke recovered per unit weight of carbon in the fuel burned, varied widely among the hydrocarbons tested, the extremes differing by a factor of 15. The smoke yields of most of the hydrocarbons and hydrocarbon derivatives correlated well with their strength as carbon acids, i.e., their tendency to dissociate to form carbanions.

Strong Lewis-acids and bases and halogen - containing flame inhibitors, as additives, increased the smoke yield of hydrocarbons. The fractional increase in smoke yield thus produced was in inverse relation to the intrinsic smoke yield of the hydrocarbon burned. An argument is given to show that the diminished fractional increase in the smoke yields of hydrocarbons of high intrinsic yield of smoke may be due in large part to the form of the correlation found between the smoke yield of hydrocarbons and their strength as carbon acids.

Oxygen-enrichment of the air supply to the burner was found to cause the smoke yield of benzene to approximately double in value. The smoke yield of cyclopentadiene increased 50 percent when supplied with oxygen-enriched air, but the effect was modest or negligible in the case of other hydrocarbons tested.

## CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT . . . . .	ii
1 INTRODUCTION . . . . .	1-1
2 SUMMARY . . . . .	2-1
3 APPROACH . . . . .	3-1
4 EXPERIMENTAL PROCEDURE . . . . .	4-1
5 SMOKE YIELDS OF PURE FUELS . . . . .	5-1
6 EFFECT OF ADDITIVES ON SMOKE YIELD . . . . .	6-1
Acids, Bases and Flame Inhibitors as Fuel Additives . . .	6-2
Oxygen as an Additive . . . . .	6-8
Cyanuric Triazide and Related Compounds as Fuel Additives . . . . .	6-12
Selected Hydrocarbons as Fuel Additives . . . . .	6-14
Triethyl Aluminum as an Additive . . . . .	6-16
The Effect of Solid Dehydrogenation Catalysts on Smoke Yield . . . . .	6-18
7 CONCLUSIONS AND RECOMMENDATIONS . . . . .	7-1
8 REFERENCES . . . . .	8-1
DISTRIBUTION . . . . .	8-2

## ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Apparatus for Measurement of Smoke Yields . . . . .	4-2
2	Variation of Smoke Yield with Air Supply Rate . . . . .	4-7
3	Correlation of Smoke Yields of Hydrocarbons with their Acidity	5-5

## TABLES

<u>Table</u>		<u>Page</u>
1	Relative Smoke Yields of Various Fuels . . . . .	5-2
2	Smoke Yields of Substituted Benzenes . . . . .	5-6
3	Effect of Acids, and Flame Inhibitors on Smoke Yield . . . . .	6-6
4	Effect of Acids, Bases, and Flame Inhibitors on Smoke Yield .	6-7
5	Maximum Smoke Yields of Various Fuels with 50 Percent $O_2$ - 50 Percent $N_2$ Gas Supply . . . . .	6-10
6	Effect of Indene, as an Additive, on the Smoke Yield of Decane	6-15
7	Effect on Smoke Yield of Combustion over Solid Catalysts . . .	6-20



#### ACKNOWLEDGEMENTS

This investigation was conducted under the guidance of Dr. Mathew G. Gibbons, Technical Coordinator, U.S. Naval Radiological Defense Laboratory (USNRDL), whose direction and assistance are gratefully acknowledged.

Much of the experimental work was performed by Mr. Trueman Farnsworth, whose skill and persistence were implemental in a major degree to the conduct of the investigation.

Technical editing was provided by Allen Saltzman.

## Section 1 INTRODUCTION

In a study conducted in 1963 under sponsorship of the Office of Civil Defense (Ref. 1) of the feasibility of countermeasures to thermal radiation produced in nuclear explosions, it was concluded that smoke screens composed of optically absorbing particles offered an effective countermeasure. In a subsequent investigation (Ref. 2) this conclusion was confirmed, and it was shown, on the basis of both theoretical and experimental results, that carbon was near optimum as a material of which to compose ground-level screens for this purpose.

Smoke generators employed in the experimental program included solid types, based on polymer fuels with potassium perchlorate incorporated as an oxidizer, and also liquid hydrocarbon fueled generators employing atmospheric air as oxidizer. Generators of both types were developed having performance characteristics capable of satisfying the requirements of a thermal countermeasure system; however, in either type of generator, any stable mode of operation required that the majority of the fuel be burned to produce heat, so that only a minor fraction of the carbon contained in the fuel was available to form carbonaceous smoke.

In circumstances requiring rapid erection of the countermeasure screen, generators capable of a high rate of smoke production must be available; however, a concomitant high rate of heat generation would be undesirable for various reasons, the most important of which is probably the fire hazard it might present under some conditions. Any improvement in the fuel efficiency of a carbon smoke generator promises a compound benefit in ameliorating this problem, because the number of pounds of fuel required to obtain any desired atmospheric loading of smoke could be reduced if the smoke produced per pound of fuel were increased, while, at the same time, less heat would be produced per pound of fuel because less of the total carbon would be burned. Additionally, improved efficiency in conversion of fuel to carbon smoke would be important to the thermal countermeasure program also in reducing fuel costs, reducing the size and cost of fuel tankage

associated with each generator, and in reducing the amount of carbon monoxide produced with the smoke.

Partial (fuel-rich) combustion of hydrocarbons in air has been given principal consideration as a process for generation of carbon smoke because hydrocarbon fuels are inexpensive, contain a high weight-percent carbon, and are available in the required quantities. Furthermore, the combustion of hydrocarbons in air can produce nearly pure carbon smoke, free of other particulate matter. The only toxic material produced in significant quantity in the combustion of hydrocarbons is gaseous carbon monoxide, which can disperse readily into the atmosphere and be reduced ultimately to negligible concentrations without permanently contaminating areas in the vicinity of the generators.

Preliminary experiments had shown that significant increases in the amount of carbonaceous smoke produced in the burning of hydrocarbon fuels in air could be obtained by choice of appropriate fuel and, in some cases, by incorporating additives in small concentration in the fuel. The present investigation was undertaken to assess the advantages of this approach that were indicated by the preliminary work.

## Section 2

## SUMMARY

An experimental investigation was conducted of the improvement in the performance of carbon smoke generators, of a type considered for use in a thermal countermeasure program, that could be obtained by choice of appropriate fuel and the introduction of additives to the fuel. The improvement of performance desired was higher recovery of fuel carbon as smoke and generation of less heat.

The smoke yield, defined as the weight of carbonaceous smoke recovered per unit weight of carbon in the fuel burned, was measured for 35 different pure hydrocarbons under closely controlled conditions in a laboratory generator. The laboratory generator was geometrically similar to one previously employed, experimentally, in the thermal countermeasure program.

The following general classes of additives were tested for their effect on the smoke yield of hydrocarbon fuels.

1. Acids and bases (electron acceptors and donors) and known flame inhibitors
2. Oxygen, in the form of oxygen-enrichment of the air supply
3. Selected hydrocarbons of high intrinsic smoke yield as additives to hydrocarbons of lower smoke yield
4. Compounds capable of initiating energetic reaction at moderate temperatures (triethylaluminum and cyanuric triazide).
5. Solid dehydrogenation catalysts

Findings were as follows:

1. The extreme values of smoke yield, of various pure hydrocarbons tested, differed by a factor of fifteen
2. A tentative correlation was discovered between the smoke yields of pure hydrocarbons and their strength as carbon acids
3. If compounds of questionable stability in long-term storage are excluded, the isomers of xylene offer the highest smoke production per unit weight of fuel of any fuel tested

4. Strong Lewis-acids and bases were found to be active in promoting increase in smoke yield; however, the increases were modest, being of the order of 35 percent or less. Halogen-containing flame inhibitors also increased smoke yield. The effectiveness of these additives has an inverse relationship to the intrinsic smoke yield of the fuel. An argument is presented to show that this inverse relationship may be a consequence of the correlation between smoke yield and carbon acid strength mentioned in item 2, above.
5.  $\text{Fe}(\text{CO})_5$  and  $\text{CrO}_2\text{Cl}_2$ , which are reported to show the highest order of effectiveness as flame inhibitors, apparently inhibit formation of smoke.
6. When the air supply to the smoke generator was enriched in oxygen to a composition 50 percent oxygen and 50 percent nitrogen, other parameters remaining unchanged, the smoke yield of benzene was increased more than a factor of two. The smoke yields of other fuels tested in the enriched air supply increased a modest amount or showed little change.
7. A solution of 5.78 weight percent of a hydrocarbon of high smoke yield (indene) in a hydrocarbon of low smoke yield (n-decane) produced a higher smoke yield by 25 to 50 percent than would have been obtained from its components if each had been burned alone, indicating indene to be active in promoting the smoke yield of n-decane.
8. An increase in smoke yield of about 20 percent was observed for fuels burning over granular, solid catalysts having acidic surfaces (activated alumina, and phosphorous pentoxide on diatomaceous earth) and over one having a basic surface (sodium amide on diatomaceous earth) compared with the same fuels burning alone.

Recommendations are:

1. Further chemical investigation intended to improve the performance of carbon smoke generators should seek an understanding of the mechanism of formation of carbonaceous smoke.
2. In the immediate term, it is recommended that an investigation be conducted of the extent to which the performance of a full-scale prototype smoke generator, employing a hydrocarbon fuel with air as oxidizer; can be improved by optimizing the mode of mixing and degree of turbulence of the streams of fuel vapor and air, for greatest production of smoke.

## Section 3

## APPROACH

The basic method of the present investigation has been the measurement and intercomparison of the smoke yields\* of a wide variety of fuels and fuel additive combinations.

The principal purpose of the smoke-yield measurements is to find the relative effect that various fuels and fuel-additive combinations would have on the smoke production of a field smoke generator. The combustion process in the measurement apparatus must therefore simulate, insofar as possible, that of the field generator, since the amount of smoke produced in hydrocarbon flames varies in different kinds of flames and burners, even for the same fuel.

In the same kind of burner system, however, the smokiness of hydrocarbon flames is known to be influenced by variables other than the properties of the fuel. For example, in flames in which the reactants have not been premixed, the smoke yield is affected by the schedule of mixing of fuel vapor and air during combustion, especially with respect to the degree of turbulence present. Differences, in successive experiments, in the pattern of heat transfer between the flame and its surroundings can affect the progress of combustion, and hence the smoke yield. This is especially so in the case of pool-burning of liquid fuels, since the rate of supply of fuel vapor to the fire by evaporation is dependent on the rate of heat transfer between flame and liquid fuel.

Variation of the smoke yield due to effects of this kind must evidently be suppressed if the variation due to fuel type and additives present is to be made apparent. Variation in the measurements due to these latter effects can be minimized or eliminated by conducting all the experiments in a combustion apparatus that is invariant in the relative position of its various parts, with accurately controlled air supply that is constant (during a given experiment)

---

\* Smoke yield is defined as the number of grams of carbonaceous smoke produced per gram of carbon contained in the fuel sample.

and reproducible in its rate, composition, and temperature and by using the same volume of fuel sample in all experiments.

The difference in behavior during combustion of different fuels burning in the same burner under uniform conditions will, hopefully, be repeated in the same kind of burner on a larger scale, although it is not to be expected that this duplication will be perfect. The variables that influence combustion behavior will not necessarily follow the same scaling laws when the linear dimensions of the burner are increased from those of the laboratory model to those of the full-scale field generator. Unfortunately, the variables that influence the smokiness of combustion do not appear to be sufficiently well established to permit these scaling relationships to be precisely specified.

It would appear, however, that the aspects of combustion most likely to change with scale would be physical effects, such as convection and degree of turbulence, whereas effects due essentially to chemical properties of the fuel would be less affected by changes in scale. Thus, the absolute value of the smoke yield, which is dependent to some extent, on the schedule of mixing of the reactants and, hence, on turbulence, would be expected to change with scale, while the relative order in which various fuels stand with respect to the smokiness of their flames - an order that is largely determined by their chemical properties - would be expected to remain invariant.

#### Section 4

#### EXPERIMENTAL PROCEDURE

The apparatus for measurement of smoke yield illustrated in Fig. 1, comprised a controlled air supply, smoke generator, and smoke collection system. The smoke generator was geometrically similar to one that had been employed previously in the thermal countermeasure program, i.e., a tray of liquid fuel surrounded by an enclosure. In the full-scale apparatus, the air supply was controlled by the size of the draft openings in the base of the enclosure. In our laboratory apparatus the air supply to the smoke generator came from a tank of compressed air, in which the pressure was automatically maintained within narrow limits by a compressor drawing atmospheric air. Air from the tank passed through a pressure regulator and microregulating control valve. The constant flow of air thus produced was passed through a copper heat exchanger coil immersed in water at room temperature, from which it passed through a rotameter for flow measurement. The air passed directly from the rotameter to the smoke generator.

The smoke generator consisted of a porcelain tray containing the fuel sample supported in the bottom of a glass chimney. The air supply flowed upward through an annular opening between the edge of the tray and a narrow baffle extending to the wall of the chimney. The relative magnitude of the various dimensions of the smoke generator were adjusted empirically until satisfactory performance was obtained and then maintained constant in subsequent experiments.\* The main

---

\* It was found that variations of the order of 10 percent in measured values of smoke yields near the maximum could result from quite minor variations in configuration in the vicinity of the tray, presumably because these variations influenced the air flow patterns and, hence, the schedule by which air entered the flame. Changes of this magnitude were produced, for example, by raising the tray relative to the air flow control baffle a distance of about 1 mm. Such changes in configuration could also produce changes in the shape of the curve of smoke yield versus air supply rate. We were concerned in this investigation exclusively with relative values of smoke yield, e.g., the smoke yield of one fuel relative to that of another or of the yield of a fuel plus additive to that of the fuel alone, so that it was sufficient simply to design the system in the vicinity of the tray so that its configuration was reproducible and constant.



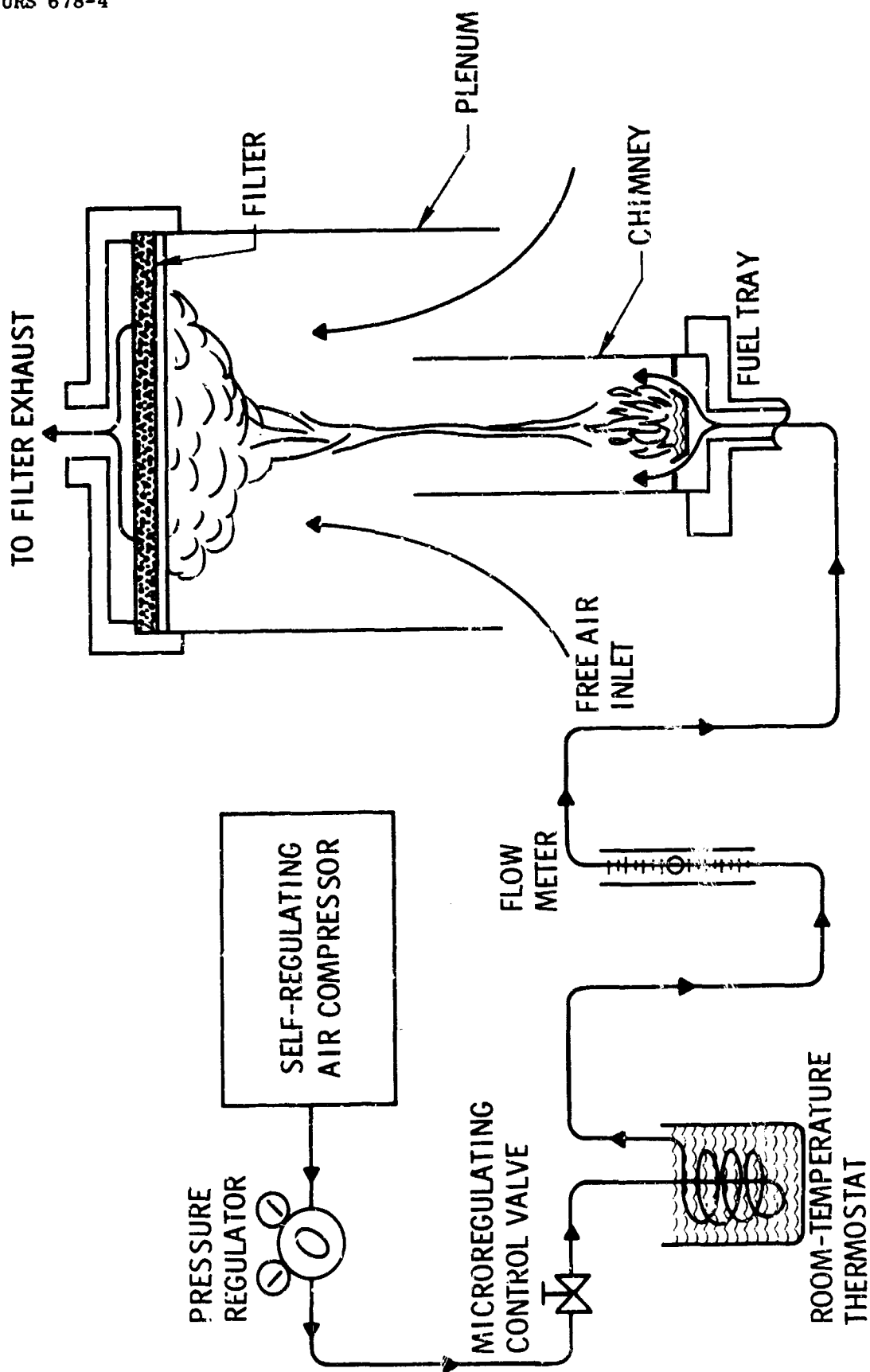


Fig. 1. Apparatus for Measurement of Smoke Yields

adjustments required were of the ratio of length to diameter of the chimney necessary to prevent ingress of air by convection down the chimney so that the air available to the flame would be established by the measured air supply rate, and to establish a configuration around the fuel tray that would ensure orderly, reproducible combustion over the tray at all air supply rates. (In some configurations, the flame flowed down over the side of the tray at the higher air supply rates to burn in an irregular fashion in the base of the chimney.)

The smoke was collected by filtration on a high-efficiency filter\* composed entirely of glass fibers. The filter, which was rated for continuous duty at a temperature of 1000°F, was supported on a sintered bronze plate. The supporting plate allowed free passage of air but was sufficiently fine-grained to prevent any of the filter mat being drawn through it into the exhaust system.

In operating the apparatus, a tared filter was placed in the filter holder, and the air supply rate was adjusted to the desired value. One cubic centimeter of fuel was charged to the fuel tray via a small hole in the side of the chimney, the filter exhaust pump turned on, and the fuel ignited by means of a miniature torch (burning natural gas and oxygen) inserted through the hole in the base of the chimney. Upon ignition, the torch was immediately removed and the hole in the chimney stoppered. Burning times were recorded with a stopwatch.

In pool-burning, the temperature of the liquid fuel is quickly brought to the vicinity of the fuel boiling point by heat transferred from the flame and remains near this temperature until the fuel is consumed. The tray in which the fuel is contained must follow, approximately, the temperature of the fuel, and thus absorbs some of the heat generated in combustion. If the fuel tray were at room temperature before each experiment, it would absorb an amount of heat that would tend to vary with the boiling point of the fuel. Furthermore, the heat absorbed by the tray is not returned into the flame, as is the heat absorbed by the fuel in its vaporization. Under these conditions, therefore, the fuel tray

---

\* Fixt-Flo air sampler filter sheet, fiber glass, Part No. 08/88332. Manufactured by Mine Safety Appliances Co., 201 North Braddock Ave., Pittsburgh, Pa., 15208.

would extract an amount of heat from the flame that would vary from one fuel to the next. The magnitude of the effect of this variable loss on the heat balance of the flame would depend on the heat capacity of the fuel tray relative to the size of the fuel sample burned, as well as on the range of boiling points of the fuels tested.

To obviate this difficulty, the fuel tray in our smoke-generating apparatus was warmed, immediately before each experiment, to a temperature 20°C lower than the boiling point of the fuel being tested. The heat capacity of the tray was approximately ten times as great as that of the fuel sample to be placed in it, so that by preheating it, the initial temperature of fuel and tray together was established, in each experiment, at nearly the same increment of temperature below the fuel boiling point. In this way, the amount of heat, generated in combustion that was absorbed in raising the temperature of the fuel and its container to the fuel boiling point was made nearly the same in each experiment.

After the fuel sample was burned the filter was removed from its holder and back-weighed to obtain the weight of smoke collected on it, after which the smoke deposited on the chimney and filter inlet plenum was removed by means of a sable brush and added to the filter sample. The filter was then weighed again to obtain the total sample weight and also the weight of the chimney deposit. Chimney deposits were commonly on the order of 10 percent of total sample weight and were nearly completely recovered by the brushing procedure, so that the unrecovered part constituted a negligible error in the smoke-yield measurement.

The quantity of fuel charged to the smoke generator (1 cc) was determined by the capacity of the filter. For example, if 2 cc of a fuel of high smoke yield were burned, the pressure drop across the filter increased, due to excessive loading, until flow into the filter was reduced to the point that some of the smoke sample was lost through the free-air inlet. This occurred even though the filter exhaust pump was a positive rotary blower capable of drawing at least 3 psi of vacuum behind the filter at low flow rates. This difficulty was not encountered when the sample volume was standardized at 1 cc.

A series of preliminary measurements were made to assess the reproducibility

to be expected in the weight of the filters under the experimental conditions to which they would be subjected in collecting smoke samples. Five measurements were made, in each of which a filter was weighed and placed in the filter holder. The filter exhaust pump was operated for 2 min in each case, but without combustion of any fuel in the smoke generator. The filters were removed and backweighed. The purpose of these measurements was to find the variation to be expected in weight of the filter alone ascribable to handling procedures. All five filters gained weight by amounts ranging from 0.1 to 1.1 mg, the average being 0.7 mg. The weight of the filters ranged from 1.3569 to 1.3796 g with an average weight of 1.3670 g. The average variation in weight of the filters was thus 0.05 percent of their weight.

Two measurements were made in which the procedure was identical to that given above, except that during each of the tests a 1-cc sample of methyl alcohol was burned in the fuel tray of the smoke generator and the combustion products drawn into the filter. Methyl alcohol produces no smoke in combustion but simulates the combustion of hydrocarbons in other respects, in that heat, water vapor, and oxides of carbon are produced. These tests were made to determine whether the passage of heated combustion products through the filter, together with the handling procedure, would affect the weight of the filter. One of the filters gained 0.3 mg; the other lost the same amount.

In the course of our subsequent experimental program, the smallest samples of carbonaceous smoke that were consistently measured were those produced by combustion of 1 cc of various normal paraffins (n-hexane, n-heptane, n-decane). These minimum samples of smoke weighed from 13 to 18 mg. The average expected error in their measurement due to variations in weight of the filter would therefore be about 5 percent. In the case of larger smoke samples, such as those produced in the burning of 1 cc of benzene, which contained 117 mg of smoke, this kind of error would be reduced to 0.6 percent.

After the reproducibility of the filter weights was established as described above, a series of preliminary smoke-yield measurements were made for the purpose of estimating the reproducibility of the smoke yield of a given fuel in successive

measurements made under identical conditions and also to explore the variation of smoke yield to be expected of various fuels as a function of air supply rate to the smoke generator. Three measurements were made of the weight of smoke obtained in burning of 1.0 cc of benzene under identical conditions.\* The average weight of smoke obtained was 115.8 mg. The maximum difference between any two smoke sample weights was 1.7 mg, and the average difference from the mean sample weight was 0.7 mg, or 0.6 percent of the mean smoke sample weight.

This order of reproducibility of the smoke yield measurements was corroborated, in the subsequent measurements of smoke yields of various fuels as a function of air supply rate, by the smoothness of the experimentally determined curves. Some of these curves are presented in Fig. 2. The curves typically show a maximum, and the maxima for most of the hydrocarbons for which curves were obtained occur at nearly the same air supply rate, viz., 4.8 liters per minute. At air supply rates below that corresponding to maximum smoke yield, the smoke usually became loaded with partially oxidized organic compounds (as indicated by odor and color) as well as being reduced in amount. Eventually, a minimum air supply rate was reached below which the flame could not be supported. As the air supply rate was increased above the rate for maximum smoke yield, the flame became more turbulent, and ultimately a condition was reached at which little or no smoke was produced.

In the intercomparison of smoke yields between different fuels and between the same fuel with different additives, it appeared desirable to use the yield corresponding to the maximum in the curve of smoke yield versus air supply rate. Since the majority of the fuels for which curves of smoke yield versus air supply rate were obtained showed maxima in these curves at or near the same air supply rate, it was appropriate to choose a single standard air supply rate at the common maximum at which to make measurements for comparison purposes. This standard was taken at 4.80 liters/min.

\* The air supply rate in these three experiments was slightly higher than that later chosen as standard.

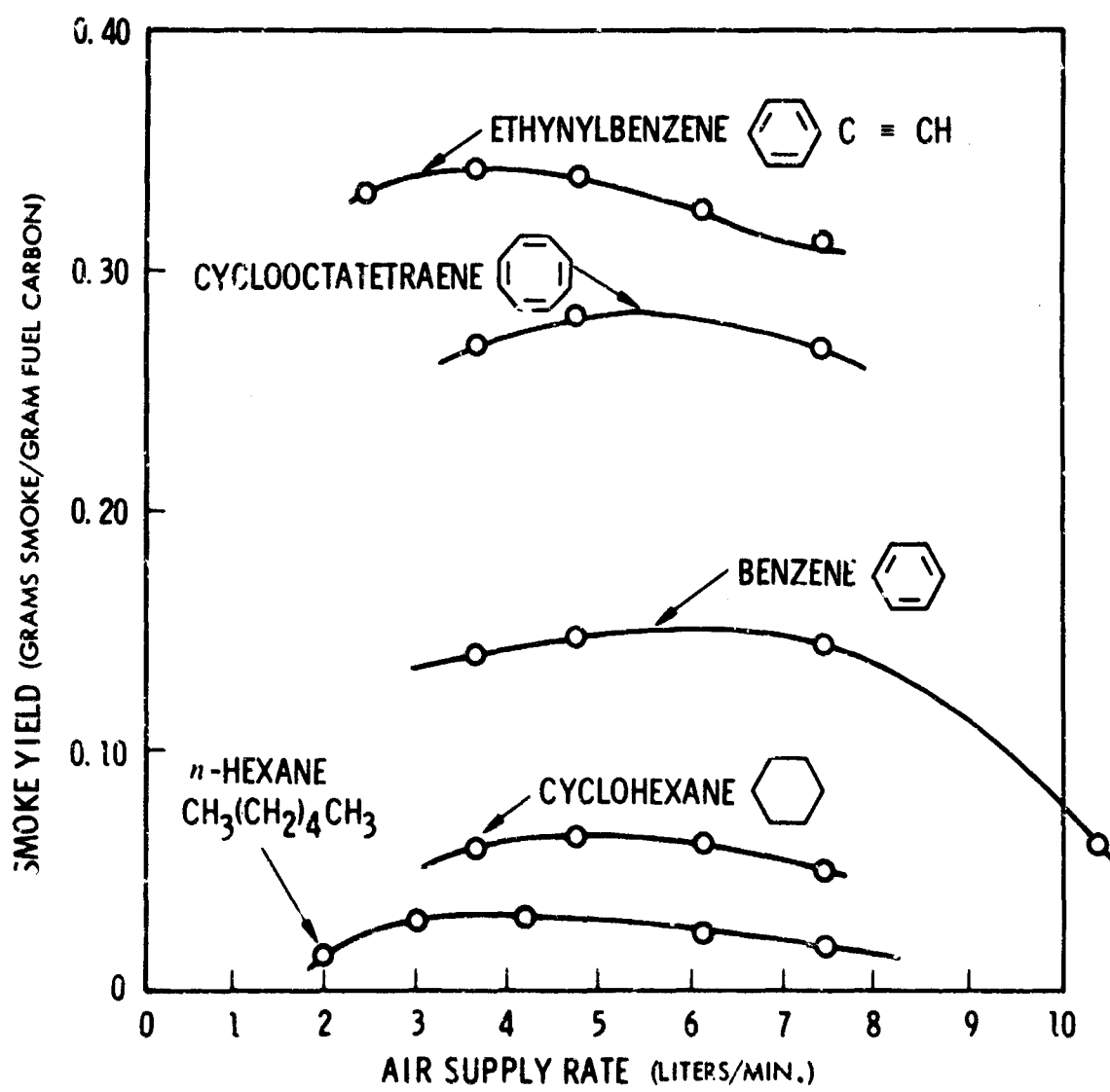


Fig. 2. Variation of Smoke Yield with Air Supply Rate

## Section 5

### SMOKE YIELDS OF PURE FUELS

The smoke yields of pure fuels for which measurements were made are arranged in Table 1 in decreasing order of yield. A correlation appears to exist between the smoke yields of hydrocarbons and their acid strength. This is illustrated in Fig. 3, in which the negative logarithms of the acid dissociation constants of those hydrocarbons for which such data are available are plotted against their smoke yield. The correlation is best for the more weakly acidic hydrocarbons. The acid constants assigned to the various hydrocarbons are those of the MSAD scale\* as given by Cram (Ref. 3, p. 19).

The acid dissociation constants plotted in Fig. 3 were measured in various non-aqueous solvent systems, whereas the reactions leading to formation of carbon smoke in combustion occur in the gas phase. The observed correlation could still be meaningful, however, since this would only require that the relative proclivity of various hydrocarbons toward acid dissociation in the gas phase be parallel to that in liquid solvents.

Additional qualitative evidence of the effect of hydrocarbon acidity on smoke yield is afforded by the relative smoke yields of various substituted benzenes. When an electron-accepting group, such as a nitro or cyano group, is substituted for hydrogen in the benzene ring, it has the effect of making adjacent hydrogens in the ring more acidic than in unsubstituted benzene. Electron donors, such as amine or hydroxyl groups, have the opposite effect; so that in aniline and phenol, ring hydrogens are less acidic than in benzene. The smoke yields of these substituted benzenes are shown in Table 2 relative to that of benzene itself.

---

\* The acid strengths of hydrocarbons are variable over such a wide range (approximately 35 to 40 orders of magnitude in the acid constant) that techniques applied in the determination of acid strength in one part of the scale are not appropriate in another. The MSAD scale of hydrocarbon acid constants has been assembled from the results of four different investigations, in different regions of the scale, employing different techniques, i.e., those of McEwan, Streitwieser, Applequist, and Desay.

Table 1  
RELATIVE SMOKE YIELDS OF VARIOUS FUELS






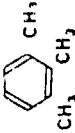
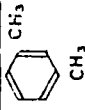
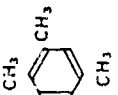
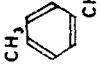
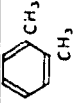
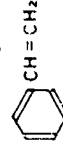

FUEL	MOLECULAR STRUCTURE	BURNING TIME (sec)	$\frac{\text{gm smoke}}{\text{gm fuel}}$	SMOKE YIELD	
				$\frac{\text{gm smoke}}{\text{gm fuel}}$	$\frac{\text{gm carbon}}{\text{gm fuel}}$
ethynyl benzene		87	0.321	0.341	
cyclooctatetraene		110	0.260	0.281	
indene		118	0.247	0.266	
dicyclopentadiene		126	0.238	0.262	
nitrobenzene		107	0.151	0.258	
1, 2, 3 - trimethylbenzene		122	0.209	0.233	
m - xylene		120	0.194	0.214	
1, 2, 4 - trimethylbenzene		119	0.191	0.213	
p - xylene		118	0.186	0.206	
o - xylene		121	0.182	0.201	
styrene		89	0.185	0.200	
cyclopentadiene		61	0.180	0.199	



Table 1 (cont.)










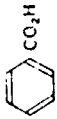






FUEL	MOLECULAR STRUCTURE	BURNING TIME (sec)	$\frac{\text{gm smoke}}{\text{gm fuel}}$	SMOKE YIELD	
				$\frac{\text{gm smoke}}{\text{gm fuel}}$	$\frac{\text{gm smoke}}{\text{gm carbon}}$
1, 2, 4, 5 - tetramethylbenzene		119	0.163	0.163	0.183
benzonitrile		131	0.148	0.148	0.181
toluene		102	0.169	0.169	0.179
cycloheptatriene		55	0.152	0.152	0.17
1, 5 - hexadiene	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$	58	0.140	0.140	0.160
quinoline		120	0.133	0.133	0.158
benzene		80	0.133	0.133	0.144
aniline		148	0.111	0.111	0.143
cyclopropane-carbonitrile		113	0.084	0.084	0.117
phenol		131	0.086	0.086	0.113
1, 3 - pentadiene	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$	43	0.088	0.088	0.099
benzoic acid		129	0.068	0.068	0.099

Table 1 (cont.)

FUEL	MOLECULAR STRUCTURE	BURNING TIME (sec)	$\frac{\text{gm smoke}}{\text{gm fuel}}$	SMOKE YIELD	
				$\frac{\text{gm smoke}}{\text{gm fuel}}$	carbon
nitrocyclohexane		148	0.050	0.092	
cyclopentane		83	0.077	0.091	
pyridine		94	0.067	0.089	
pyrrole		103	0.057	0.079	
benzoquinone		135	0.041	0.071	
2, 2, 3 - trimethylbutane	$\text{CH}_3 \text{ C}(\text{CH}_3)_2 \text{ CH}(\text{CH}_3) \text{ CH}_3$	80	0.056	0.066	
cyclohexane		101	0.054	0.063	
n - hexane	$\text{CH}_3 (\text{CH}_2)_4 \text{ CH}_3$	85	0.026	0.031	
n - nonane	$\text{CH}_3 (\text{CH}_2)_7 \text{ CH}_3$	95	0.026	0.031	
n - decane	$\text{CH}_3 (\text{CH}_2)_8 \text{ CH}_3$	168	0.024	0.029	
n - heptane	$\text{CH}_3 (\text{CH}_2)_5 \text{ CH}_3$	100	0.021	0.023	

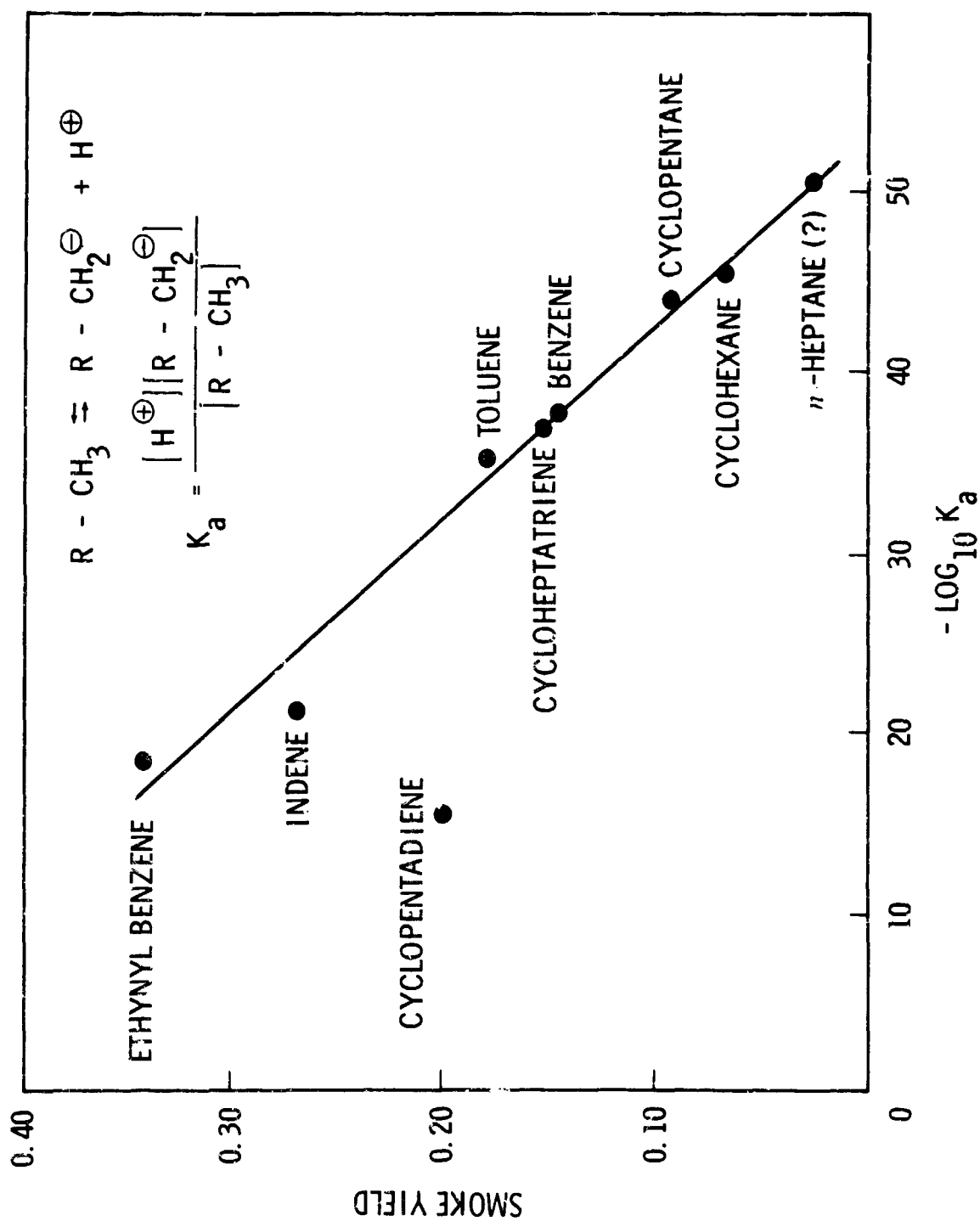
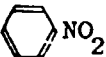
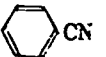

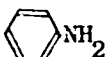
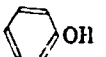


Fig. 3. Correlation of Smoke Yields of Hydrocarbons with their Acidity

Table 2  
SMOKE YIELDS OF SUBSTITUTED BENZENES

COMPOUND	STRUCTURE	SMOKE YIELD RELATIVE TO THAT OF BENZENE
nitrobenzene		1.79
benzonitrile		1.26
benzene		1.00
aniline		0.99
phenol		0.78

The relative smoke yields of the benzene derivatives listed in Table 2 thus stand in the same order as the acidity of the hydrogen atoms attached to their benzene rings.

The smoke yield of toluene is higher than that of benzene, even though the methyl substituent renders the hydrogen atoms of its benzene ring less acidic than in benzene, because, as remarked by Shatenshtein (Ref. 4, p. 196), the hydrogens of the methyl group itself, in toluene, are more acidic than those of benzene.

The acid dissociation constants of compounds such as benzoic acid, phenol, and aniline are several orders of magnitude greater than those of any of the hydrocarbons, but they produce only modest smoke yields. Similarly the simpler alcohols, which do not appear in Table 1 because their smoke yields are either zero or too low to be of interest, are more acidic than hydrocarbons. In all of these cases, however, these higher acid constants refer to the dissociation of hydrogen attached to oxygen or nitrogen instead of carbon. From this observation, it would be inferred that the smokiness of the flame does not depend on the dissociation of the positive hydrogen ion, but rather on the formation of a negatively charged hydrocarbon ion (carbanion) having its charge associated with carbon.

Two apparent exceptions to the correlation of smoke yield with hydrocarbon acidity have occurred that have resisted any resolution. The first of these is the low smoke yield of cyclopentadiene, evident in Fig. 3. The second consists of the high smoke yield of 2, 2, 3 - trimethylbutane relative to that of n-heptane. These compounds are isomers, their difference residing solely in the branched structure of the former, compared to the straight-chain configuration of the latter. The acidity of alkanes is reported to be lower in branched than in normal isomers (Ref. 4, pages 96 and 195, and Ref. 5). The smoke yield of 2, 2, 3 - trimethylbutane, however, is nearly three times as great as that of n-heptane, a result in accordance with the findings of other investigators (Ref. 6, page 271), but just the opposite of that to be expected if smoke yield parallels hydrocarbon acidity.

Referring to Table 1, it is seen that if fuels of questionable chemical stability in long-term storage are excluded, the xylenes and trimethylbenzenes produce the highest weight of smoke per unit weight of fuel. At a current price of about \$0.035 per pound, (\$0.25 per gallon), mixed xylene isomers also offer the advantage of being relatively inexpensive. Dicyclopentadiene offers a 25-percent greater smoke production per pound of fuel than the xylenes, but it is more expensive (currently \$0.12 per pound) and its stability in storage is not known.

The naturally occurring mixture of xylene isomers begins to freeze at about  $-30^{\circ}\text{C}$  ( $-22^{\circ}\text{F}$ ), so that, as a fuel, it can be expected to remain a liquid under most outdoor storage conditions.

## Section 6

### EFFECT OF ADDITIVES ON SMOKE YIELD

The quality desired of fuel additives in the present investigation was that, when added to a fuel in small concentration (5 weight percent or less), they would produce a substantial increase in the smoke yield of the fuel. The belief that this might be possible was based on the observation that all of the hydrocarbons eligible for consideration as practical fuels for carbon smoke generators are thermodynamically unstable with respect to decomposition into carbon and hydrogen at room temperature as well as at higher temperatures characteristic of flames. Furthermore, many of the unsaturated hydrocarbons are exothermic with respect to decomposition into carbon and hydrogen.

The fact that these hydrocarbons ordinarily do not form carbon particles at temperatures below about 1000°C, either in combustion or pyrolysis, must therefore be attributed to the existence in the reaction mechanism of steps requiring a large investment of energy for their completion. The high temperature would then be required to provide a ready source of energy to drive the reaction over the energy barriers represented by these intermediate steps, even though the overall reaction is thermodynamically feasible at lower temperatures.

An additive capable of changing the reaction mechanism leading to formation of smoke to one in which less energetic intermediate steps were involved could, therefore, induce the formation of smoke at a lower temperature. In combustion, then, less of the carbon would need to be burned to maintain the temperature of the flame, so that a larger fraction of the carbon would be available to make smoke.

Other approaches to the catalysis of smoke production would appear to be possible. The heat produced in the oxidation of the hydrogen, contained in hydrocarbon fuels, to water would be more than sufficient to maintain flame temperature, even if none of the carbon were oxidized. At the equilibrium toward which the system tends at the temperature of the flame, however, just the opposite

situation prevails, i.e., virtually all of the short supply of oxygen would be combined with carbon in the form of carbon monoxide, while nearly all the hydrogen would remain unoxidized. Flames, however, are dynamic systems, and the compositions of their final products are apt to be the result of the relative rates of competing reactions, without equilibrium ever being reached. Thus, an additive capable of influencing relative reaction rates in a direction resulting in oxidation of more hydrogen and less carbon would increase smoke production without the need of any reduction in flame temperature.

The formation of smoke can hardly be a simple reaction, since it involves the conversion of relatively small hydrocarbon molecules containing one or two hydrogen atoms per carbon atom into carbonaceous particles of smoke containing on the order of  $10^4$  to  $10^9$  carbon atoms, with only about one hydrogen atom remaining for each eight carbons. Moreover, the milieu in which the smoke-forming reaction occurs is the flame, the detailed chemistry of which is, itself, only vaguely defined at present. In searching for additives to improve the smoke yields of hydrocarbon fuels, therefore, it has been necessary to follow a heuristic approach.

#### ACIDS, BASES AND FLAME INHIBITORS AS FUEL ADDITIVES

In view of the tentative correlation between the smoke yield of hydrocarbons and their acidity, discussed earlier in this report, acids and bases (in the sense of being electron acceptors or donors) have been tested as additives. The rationale was that if the smoke-producing process depended in an important way on the acid dissociation of the hydrocarbon fuel, the addition of strong acids or bases could promote this dissociation by suppressing the activity of one or the other of the products of the dissociation or, in the case of acids, by inducing greater acidity in the fuel molecule by formation of coordination complexes with it. The interpretation of some of the experiments, involving Lewis-acids as additives, was obfuscated because some of the stronger acids were relatively volatile compounds of metallic elements, usually a halide, that were capable of forming nonvolatile compounds by hydrolysis or by reaction with oxygen. Any of the acid that was converted to metal oxide or hydroxide in passing through

the flame would condense, owing to its lower volatility, and deposit with the smoke in the filter, whereas the additive in its original more volatile form would pass through the filter as a vapor with the gaseous combustion products.

A question common to these experiments was, therefore, how much, if any, of the increase in apparent weight of the smoke sample collected in the filter was metal oxide, hydroxide, or oxohalide formed by hydrolysis of the additive in the flame or in the products of combustion prior to their reaching the filter. Prediction of the amount of metal oxide deposited in the filter in these experiments was often plagued by uncertainty as to whether all of the metal-containing additive had evaporated from the fuel tray with the fuel, as well as the question of whether all of the vaporized additive that did accompany the fuel into the flame was, in fact, hydrolyzed and condensed to solids before reaching the filter.

Quantitative measurement of the amount of metal oxide deposited in the filter was needed in these cases. The analytical problem was not severe, in that only one kind of metal was present in each instance and its identity was known beforehand. Analytical determination of the metal oxide present in each filter was complicated from an operational point of view, however, by the circumstance that a different metal was involved in each of this kind of acidic additive tested, so that a different analytical procedure, suitably reconciled to the presence of the glass fiber filter and carbonaceous solids, would need to be adapted for the metal contained in each additive.

Quantitative analysis for the carbon content of the smoke samples was a possible alternative. Insofar as the weight of carbonaceous smoke in the filter sample could be taken equal to the weight of carbon found in analysis, the desired answer would be given directly. It offered the advantage that the same procedure could be applied to all samples irrespective of the nature of the metal oxides contained in them, however it suffered some disadvantage in that carbonaceous smoke is not composed solely of carbon, but contains at least 1 percent by weight of hydrogen chemically bonded in its structure, as well as variable amounts of oxygen and, in some cases nitrogen, if that element is present



in the fuel. Thus the analysis for carbon, in addition to being somewhat tedious, is also incapable of providing exact determination of the weight of carbonaceous smoke in the filter sample.

A simple, rapid, gravimetric method was adopted for measurement of the amount of metal oxide contained in the filter samples, one which is essentially independent of the kind of metal oxide present. The method depends on oxidation of the carbonaceous smoke on the filter by an oxygen plasma containing a high proportion of oxygen atoms. The oxygen plasma was formed by microwave discharge in oxygen at reduced pressure. Atomic oxygen reacts with organic material and carbon with negligible activation energy, so that oxidation can proceed at room temperature, the rate being determined by the rate of delivery of oxygen atoms to the carbonaceous material. Although the electrons in the plasma are at a high temperature, they are not in temperature equilibrium with the oxygen atoms, which remain near ambient temperature. Oxidation of the carbonaceous smoke proceeds quantitatively to completion in approximately 30 min to 1 hour without raising the temperature of the sample more than a few degrees above room temperature. Owing to the mild thermal conditions, and the insignificant chemical effect of the plasma on the glass filter, its weight is not significantly altered by this treatment. Backweighing of the filter after the treatment, therefore, provides both the weight of the carbonaceous smoke and of the metal hydrolysis products present on the filter, since the tare and gross weights of the filter sample are known.

A potential source of ambiguity in the method can arise from the question of whether or not the metal had been oxidized to a higher valence state by the oxygen atoms, with consequent change in molecular composition and apparent weight. In a majority of cases in which the method has been used, it was known that the metal was in its highest oxidation state before treatment (e.g., boric acid derived from hydrolysis of boron trifluoride additive). In cases where this is not surely known, the difference between the weights of the metal oxide or hydroxide in the different oxidation states would usually constitute a minor percentage of its weight in either state, so that the magnitude of this uncertainty would not be large.

Unfortunately, this procedure was adopted so late in our program that it was not possible to apply it to all of the samples to which its application would have been useful; however, it has been applied in the case of one fuel, benzene, for each of the most strongly acidic additives which have the greatest propensity toward reaction with water or oxygen to form compounds of low volatility. The results of experiments with these additives must account for the additive deposited in the filter, so they are given separately (in Table 3) from the results for the remainder of the acidic and basic additives (given in Table 4).

Many of the chemicals that are known to inhibit the propagation of flames in hydrocarbon-air mixtures are acids (electron acceptors) or dissociate in the flame to produce acidic radicals, and some of the more strongly acidic additives in Table 3 are known to be effective as flame inhibitors. In the present investigation the results obtained concerning the effectiveness of other flame inhibiting compounds in increasing smoke production have therefore also been included in Tables 3 and 4.

Referring to Table 3, it would appear that in the cases of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ,  $\text{SbCl}_5$ , and  $\text{C}_6\text{H}_5\text{POCl}_2$ , not all of the additive, in each case, was collected as a nonvolatile hydrolysis product in the filter. The amount of noncarbonaceous residue, found in the experiment with  $\text{SnCl}_4$  as additive, agrees quite closely with the weight of  $\text{SnO}_2$  that would correspond to the total weight of additive. In the case of  $\text{CrO}_2\text{Cl}_2$ , the noncarbonaceous residue exceeds the maximum calculated in the form of  $\text{Cr}_2\text{O}_3$  by about 25 percent.

It is interesting to note that a smaller amount of noncarbonaceous residue apparently occurs in the burning of n-decane than in the case of benzene and xylene. Thus, with 5 percent  $\text{SnCl}_4$  as additive in benzene, an amount of residue equivalent (as  $\text{SnO}_2$ ) to the total amount of additive was deposited in the filter sample, whereas when n-decane containing 5 percent  $\text{SnCl}_4$  was burned, the net weight of the entire sample obtained in the filter was less than the weight of  $\text{SnO}_2$  equivalent to the  $\text{SnCl}_4$  additive. Since it was obvious from the black color of this sample that it contained some carbonaceous material, it must

Table 3  
EFFECT OF ACIDS, AND FLAME INHIBITORS ON SMOKE YIELD  
Additives Depositing Non-Carbonaceous Residues in the Filter Sample

Additive	Boiling Point (°C)	Fuel	% Additive In Fuel (vol %)	Weight of Non-Carbonaceous Residue in Filter Samples		Net Weight of Filter Sample (g)	Smoke Yield of Fuel With Additive Relative to That of Pure Fuel		Burning Time of Fuel With Additive Re- lative to that of Pure Fuel
				Estimated Max- imum Based on Total Weight of Additive (g)	As Deter- mined by Analysis (g)		Estimated Min- imum Assuming Total Additive in Filter Sample	As Determined by Analysis for Non- carbonaceous Re- sidue	
Acids	125.7	m-xylene	5	0.0193 as H <sub>3</sub> BO <sub>3</sub>	0.0073	0.1856	1.03	1.35	0.88
		benzene	5	0.0193 as H <sub>3</sub> BO <sub>3</sub>		0.1569	1.23		1.17
		n-hexane	5	0.0193 as H <sub>3</sub> BO <sub>3</sub>		0.0230	0.23		1.00
	114.1	m-xylene	5	0.0044 as SnO <sub>2</sub>	0.0688	0.2478	1.15	1.33	0.87
		benzene	5	0.0044 as SnO <sub>2</sub>		0.2133	1.34		1.11
		decane	5	0.0044 as SnO <sub>2</sub>		0.0609	----		0.61
Flame Inhibitors	79 (at 22 mm Hg)	benzene	1	0.0123 as SnO <sub>2</sub>	0.0250	0.1533	1.21	1.30	0.85
		benzene	1	0.0129 as SnO <sub>2</sub>		0.0222	0.52		0.77
		decane	5	0.0840 as Sb <sub>2</sub> O <sub>5</sub>		0.1431	0.75		0.69
	258	m-xylene	5	0.0640 as Sb <sub>2</sub> O <sub>5</sub>	0.0213	0.1499	0.77	1.17	0.76
		benzene	5	0.0640 as Sb <sub>2</sub> O <sub>5</sub>		0.0370	----		0.82
		decane	5	0.0840 as Sb <sub>2</sub> O <sub>5</sub>		0.1642	1.17		0.90
Flame Inhibitors	117	benzene	5	0.0345 as H <sub>3</sub> PO <sub>4</sub>	0.0301	0.0256	----	0.77	0.48
		n-decane	5	0.0345 as H <sub>3</sub> PO <sub>4</sub>		0.1444	0.87		0.97
		benzene	5	0.0469 as Cr <sub>2</sub> O <sub>3</sub>		0.0378	----		0.63
	103	m-xylene	4.76	0.0208 as iron	0.0208 as iron	0.1613	0.84	0.75	0.85
		benzene	4.76	0.0208 as iron		0.1369	0.39		0.97
		n-hexane	4.76	0.0208 as iron		0.0338	0.76		1.00

Table 4  
EFFECT OF ACIDS, BASES, AND FLAME INHIBITORS ON SMOKE YIELD

Additive	Boiling Point (°C)	Fuel	Concentration of Additive in Fuel	Smoke Yield of Fuel With Additive Relative to That of Pure Fuel	Burning Time of Fuel With Additive Relative to That of Pure Fuel
$ZnCl_2$	732	m-xylene	5 wt %	1.03	0.96
		nitrobenzene		1.09	1.15
		benzene		1.13	1.00
$FeBr_3$	Sublimes with decomp'n	m-xylene	5 wt %	0.98	0.86
		benzene		1.10	0.95
		n-decane		0.51	0.79
$AgClO_4$	Decomposes at 486	m-xylene	5 wt %	1.05	0.92
		benzene		1.05	0.97
		n-decane		0.39	0.74
$ZrCl_4$	Sublimes 331	m-xylene	5 wt %	1.05	0.82
		nitrobenzene		1.09	0.99
		benzene		1.12	0.99
$MoCl_5$	268	m-xylene	5 wt %	1.01	0.94
		nitrobenzene		0.93	1.05
		benzene		0.95	0.80
$WCl_6$	346.7	m-xylene	5 wt %	0.92	0.86
		nitrobenzene		1.04	1.10
		benzene		1.08	0.85
$VOCl_3$	126.7	m-xylene	10 vol %	0.78	0.40
		nitrobenzene		0.89	1.29
		benzene		1.18	0.55
$VCl_3$	Decomposes	m-xylene	5 wt %	1.00	0.83
		nitrobenzene		1.17	1.27
		benzene		1.11	1.09
$TaCl_5$	242	m-xylene	5 wt %	1.05	0.94
		nitrobenzene		1.07	1.15
		benzene		1.16	1.11
$H_2NCH_2CH_2CH_2NH_2$ $NH_2N(CH_3)_2$	135.5	benzene	5 vol %	1.17	
	63.9	benzene		1.14	
$CH_3CH_2CH_2I$	102.4	benzene	5 vol %	1.16	1.14
		n-decane		1.78	0.71
$CCl_4$	76.8	m-xylene	4.75 vol %	1.10	0.94
		benzene		1.32	1.14
		n-decane		1.65	1.10
		n-hexane		1.99	0.87
$Br_2$	58.78	ethynylbenzene	5 vol %	1.06	0.95
		benzene		1.15	1.06
		n-hexane		3.62	0.82
$CBr_4$	189.5	m-xylene	5.5 wt %	1.25	0.91
		benzene	6.5 wt %	1.28	0.94
		n-decane	7.3 wt %	3.10	0.80
		n-hexane	7.3 wt %	3.31	0.92

have contained substantially less weight of tin compounds than deposited in the filter sample obtained with benzene as fuel. A similar situation appears to prevail in the cases of n-decane with  $\text{C}_6\text{H}_5\text{POCl}_2$  and  $\text{CrO}_2\text{Cl}_2$ .

Strong Lewis-acids were found to be consistently active additives, in promoting increase in smoke yield, however the increases were modest, being of the order of 35 percent or less. The two basic additives tested increased the smoke yield of benzene. It is interesting to note that these basic additives, when burned alone as fuels, produced no trace of carbonaceous materials, either in the form of smoke or of deposit in the fuel tray.

Halogen-containing flame inhibitors were effective in increasing smoke yield. Their effectiveness appears to bear an inverse relationship to the smoke yield of the fuel without additive, however, being highest for n-hexane and n-decane and least for m-xylene and ethynylbenzene.

The flame inhibitors  $\text{Fe}(\text{CO})_5$  and  $\text{CrO}_2\text{Cl}_2$ , which are reported to show the highest order of effectiveness as flame inhibitors, apparently inhibit formation of smoke.

#### OXYGEN AS AN ADDITIVE

Some measurements of smoke yields were made in which gas composed 50 percent of oxygen and 50 percent of nitrogen, or 100 percent of pure oxygen, was substituted for the atmospheric air normally supplied to the burner. Other than the composition of the gas, all other aspects of these smoke yield measurements remained unchanged. The reasoning that prompted our undertaking these experiments was as follows.

Nitrogen, composing about 79 percent of atmospheric air, enters a diffusion flame along with the oxygen, but does not participate chemically in the combustion to any significant extent. The nitrogen must be heated to the flame temperature, however, and calculations have indicated that a substantial fraction of the heat that must be generated, to maintain flame temperature, is absorbed by nitrogen. It appeared, therefore, that if the flame were fed with

a smaller quantity of a more oxygen-rich mixture than air, some of the carbon in the fuel otherwise burned to heat nitrogen to flame temperature might be available for conversion into smoke and the smoke yield thereby increased. At the same time, the possibility was also anticipated that the higher oxygen concentration of the enriched gas might react more rapidly with the carbon smoke formed in the flame, with a consequent reduction in smoke yield compared with the case in which the flame is supplied with air. It was therefore expected that, if higher smoke yields were observed with enriched gas supply, they would occur at the lower gas supply rates, possibly, one at which the rate of oxygen delivery to the burner was similar to that contained in the air at our standard air supply rate.

All the fuels tested showed an increased smoke yield when supplied the oxygen-enriched gas, with the exception of ethynylbenzene, which gave a lower yield of smoke than with air. The increased smoke yields occurred when the oxygen-enriched mixture was admitted to the burner at our standard supply rate for air, as well as at the lower supply rates. In the special case of benzene, measurement was made at supply rates of 50 percent  $O_2$  - 50 percent  $N_2$  up to twice as high as our standard air supply rate, the yield of smoke remaining extraordinarily high over the whole range. The results are summarized in Table 5, in which the highest smoke yields observed at any supply rate of 50 percent  $O_2$  - 50 percent  $N_2$  are tabulated for each fuel tested, together with their burning times. The ratios of these quantities to those observed for the same fuels with atmospheric air supply are also included.

The enriched gas supply produced a remarkable change in the smoke yield of benzene, approximately doubling it over a wide range of gas supply rates. A similar, but less spectacular, effect was obtained for cyclopentadiene. The increase for other fuels was modest or negligible. It appears that the increase in smoke yield of the benzene flame, when supplied with oxygen-enriched gas, may be principally in the nature of a catalytic effect of the oxygen because the effect persists at high gas supply rates, and the visual appearance of the flame and apparent structure of the smoke produced are changed from those characteristic of the flame when supplied with air.

Table 5  
MAXIMUM SMOKE YIELDS OF VARIOUS FUELS  
WITH 50 PERCENT O<sub>2</sub> - 50 PERCENT N<sub>2</sub> GAS SUPPLY

FUEL	GAS SUPPLY 50 PERCENT O <sub>2</sub> - 50 PERCENT N <sub>2</sub>		RATIO OF EFFECTS MEASURED WITH 50 PERCENT O <sub>2</sub> - 50 PERCENT N <sub>2</sub> TO THOSE WITH STANDARD AIR SUPPLY	
	MAXIMUM SMOKE YIELD (gm smoke/gm fuel carbon)	BURNING TIME (sec)	MAXIMUM SMOKE YIELD	BURNING TIME
ethynylbenzene	0.327	50	0.96	0.57
benzene	0.305	32	2.12	0.40
cyclopentadiene	0.301	43	1.51	0.70
m-xylene	0.285	51	1.33	0.42
indene	0.284	78	1.07	0.66
styrene	0.209	54	1.05	0.61
n-hexane	0.037	46	1.19	0.54

The enriched gas supply produced a remarkable change in the smoke yield of benzene, approximately doubling it over a wide range of gas supply rates. A similar, but less spectacular, effect was obtained for cyclopentadiene. The increase for other fuels was modest or negligible. It appears that the increase in smoke yield of the benzene flame, when supplied with oxygen-enriched gas, may be principally in the nature of a catalytic effect of the oxygen because the effect persists at high gas supply rates, and the visual appearance of the flame and apparent structure of the smoke produced are changed from those characteristic of the flame when supplied with air.

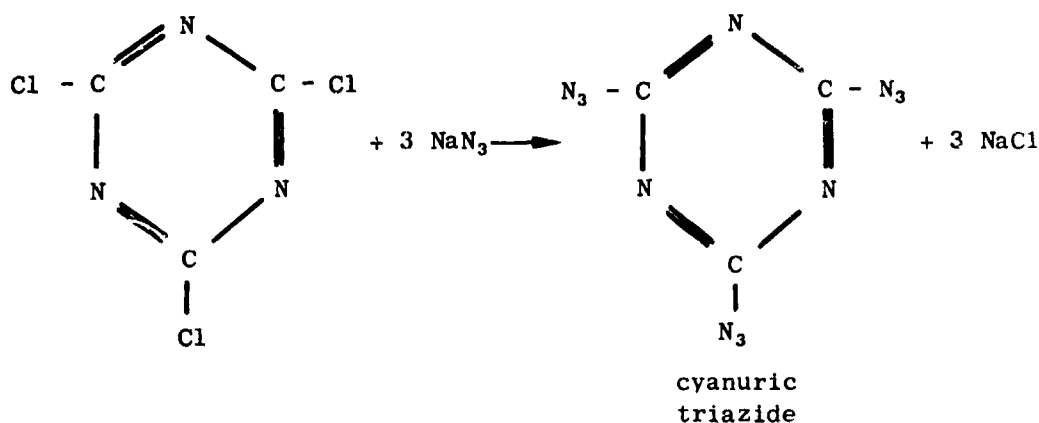
The use of pure oxygen to support the benzene flame produced only an additional 10-percent increment in the smoke yield over that obtained with 50 percent oxygen.

The practicability of supplying oxygen-enriched air to field smoke generators being doubtful, the effect was not further investigated. It became a question of much interest, however, whether a similar effect on the smokiness of benzene flames might be produced by adding an oxygen-rich compound to the fuel. The additive would need to contain a large percentage of oxygen, be soluble in benzene, and of volatility comparable to benzene so that in pool-burning of a benzene solution, it would vaporize and be carried into the flame with the fuel. Tetranitromethane (65.3 weight percent oxygen, boiling point  $126^{\circ}\text{C}$  at 760 mm Hg) fulfilled these requirements the best of any commonly available chemical. Tetranitromethane is capable of forming explosive mixtures with hydrocarbons when present in high concentrations. Preliminary experiments showed that even in dilute solutions (.05 cc tetranitromethane to 1.0 cc benzene), tetranitromethane was concentrated in the remaining liquid as burning progressed, because its volatility is lower than that of benzene, with the result that the combustion ended with a small explosion. Toluene and xylene, having boiling points more nearly that of tetranitromethane, did not present this difficulty, and it was possible to safely burn solutions containing 0.8 cc of tetranitromethane in 1.0 cc of these fuels. No increase in smoke yield resulted when these solutions were burned with standard air supply, however, the yield being slightly lower than that of the pure fuel.



## CYANURIC TRIAZIDE AND RELATED COMPOUNDS AS FUEL ADDITIVES

Cyanuric triazide is a white, crystalline solid which melts at 94°C. It is conveniently prepared from cyanuric trichloride and sodium azide by the following reaction (Ref. 7 and 8).



Cyanuric triazide is moderately soluble in benzene. The pure solid is explosive, and detonates on being heated to a temperature of 170 to 200°C, but as a fuel additive it would be present in dilute solution, and it was anticipated that, in this form, the compound might decompose in a more orderly way when subjected to heating.

Upon decomposition, pure cyanuric triazide has been shown (Ref. 7) to be converted quantitatively into cyanogen and nitrogen. In dilute solution in a fuel, however, where each molecule of the azide was surrounded, on average, only by fuel molecules, only two of the three cyano groups, forming the ring in the molecule, could be accommodated in the formation of a cyanogen molecule, so that at least one cyano free radical would be set free in the fuel for each cyanuric triazide molecule decomposed. Furthermore it would appear that these radicals would carry with them some of the energy released in decomposition of the azide molecule, and should therefore be chemically active.

Cyanogen and cyano compounds are similar in their chemical behavior to the corresponding halogen compounds to such an extent that they are referred to in chemistry texts as pseudohalogens. The effect of these compounds on the smoke yield of fuels was therefore of interest in view of the activity, in this respect, shown by halogens. Cyanogen itself is not suitable as a fuel additive since it is a poisonous gas (boiling point,  $-21.17^{\circ}\text{C}$ ). Cyanogen is inflammable, however, so that it is reasonable to expect that most of that formed in the combustion process by decomposition of cyanuric triazide would be oxidized to non-poisonous products before leaving the flame.

Smoke yields of a 10 percent cyanuric triazide solution in nitrobenzene and of 5 percent solutions in m-xylene and in benzene were measured. The burning of the m-xylene and benzene solution were uneven, being punctuated by popping and minor explosions. This roughness of burning was most prominent in the case of benzene, the lowest-boiling of the fuels tested, and was negligible in the highest-boiling fuel, nitrobenzene.

The smoke yields of the nitrobenzene and m-xylene solutions of cyanuric triazide were increased 13 percent and 11 percent respectively over the pure fuels, while the benzene solution produced only 93 percent as high a smoke yield as that of pure benzene.

Metal azides and organic azido compounds generally decompose at moderate temperatures ( $300^{\circ}\text{C}$  or less). The azido group is converted into  $\text{N}_2$  molecules, leaving the remainder of the azido compound as a free radical. These compounds would therefore appear to offer a general means for introducing different specific kinds of free radicals into combustion reactions for experimental purposes, by simply adding the appropriate azido compound to the fuel. In the present investigation, this opportunity was limited by the circumstance that azido compounds tend to be of low volatility relative to their molecular weight, and, owing to their thermal sensitivity, would be likely in many cases to decompose in the fuel tray rather than vaporizing into the flame. Azido

---

\* This limitation would not be present in some kinds of burners, for example those in which the fuel is sprayed into the flame.

compounds do not appear to be available in any wide variety commercially, so that in general it would be necessary to invest the time and labor necessary for synthesis of an azido compound of interest prior to conducting experiments with it.

#### SELECTED HYDROCARBONS AS FUEL ADDITIVES

Three measurements were made of the smoke yield of a 5.78 weight percent solution of indene in decane. The results were compared with the sum of the yields that would have been obtained, from the amounts of each hydrocarbon present in solution, if they had been burned alone.

The purpose of these measurements was to determine whether the presence of a small proportion of a hydrocarbon of high smoke yield (indene) would influence the smokiness of a fuel of low yield (decane), or if the smoke-producing functions of both fuels were essentially independent of one another. The same measurements were made at each of three different air supply rates, and the results are summarized in Table 6.

The results indicate that a higher smoke yield is obtained from the solution than would have been obtained from its components if each had been burned in pure form. Since the increased yield appears in all three tests, it is presumed that the effect is real, and that the component having the higher smoke yield (indene) promotes the formation of smoke by the component of lower yield (decane). In this sense, the indene can be thought of as an additive to improve the smoke yield of the decane.

A detailed, quantitative, intercomparison of the smoke yields of mixtures of various hydrocarbons, in various proportions, appears to be a promising means of gaining insights into the properties of hydrocarbons that are responsible for smokiness in burning. The subject was not pursued further in the present investigation, however, because the fuels tested in the present investigation, that have higher smoke yields than the xylenes, and therefore might be expected to improve the smoke yield of xylene, if present as an additive, are all of questionable stability in long-term storage, either in the

Table 6  
EFFECT OF INDENE, AS AN ADDITIVE, ON THE SMOKE YIELD OF DECANE

AIR SUPPLY RATE (liters/min)	SMOKE YIELDS			D	C/D
	A	B	C		
	PURE INDENE	PURE DECANE	5.78 WEIGHT PERCENT SOLUTION OF INDENE IN DECANE		
3.55	0.2603	0.0216	0.0567	6.34%* A 93.66%* B	RATIO OF SMOKE YIELD OF 5.78 WEIGHT PERCENT SOLUTION OF INDENE IN DEC- ANE TO YIELD THAT WOULD HAVE BEEN OB- TAINED IF THE PURE COMPON- ENTS HAD BEEN BURNED, EACH ALONE
4.80	0.2659	0.0205	0.0443	0.0367	1.54
6.10	0.2509	0.0135	0.0432	0.0360	1.23
				0.0285	1.51

\* The smoke yield has been defined as the grams of carbonaceous smoke per gram of carbon contained in the fuel sample. The appropriate fractions of the smoke yields of pure indene and pure decane, for computation of the sum of the independent yields, are therefore not the respective weight fractions of the two components in the solution, but, rather, the fraction of total carbon contained in the sample of solution that is incorporated in one component or the other.

pure form or in solution, so that the likelihood of an immediate practical advantage appearing in this direction seemed small.

#### TRIETHYL ALUMINUM AS AN ADDITIVE

As a pure compound, triethyl aluminum,  $(C_2H_5)_3Al$ , takes fire spontaneously in air and explodes when placed in contact with water or other oxygen-bearing compounds. The compound is soluble in hydrocarbons, and is stable in these solutions as long as air or compounds containing oxygen, halogens, or other reactive substituents are not present. The decision to test it as a fuel additive was chiefly the result of the belief, based on consideration of relative free energy change in the reactions involved, that if oxygen (as air) was supplied to a hydrocarbon solution of triethyl aluminum in a quantity that was only sufficient to convert the aluminum to aluminum oxide, the aluminum would prevail in the competition for the limited oxygen supply, and a negligible quantity of carbon would be oxidized. The potential advantage of such a system would stem from the fact that carbon monoxide is a major product of the fuel-rich oxidation of pure hydrocarbons\* and that the oxidation of a gram of aluminum, in the form of triethyl aluminum, to aluminum oxide releases more than three times the energy that a gram of carbon does in being oxidized to carbon monoxide. The oxidation of aluminum would, therefore, provide a much more efficient source of heat needed to maintain the temperature of the fuel-rich combustion than would oxidation of carbon, and, in addition, the considerable fraction of carbon normally turned into a poisonous oxidation product (carbon monoxide) would be available for conversion into smoke. Other advantages that appeared possible were that a pyrophoric fuel additive might stabilize the fuel-rich flame, making it less susceptible to being blown out by wind currents or shock waves, and that alkyl aluminum compounds might also exert a catalytic effect on smoke production.

A supply of triethyl aluminum diluted to a 20-percent solution in benzene was used in initial experiments. The solution is less reactive than the pure

\* It would be the only oxidized product if the process reached equilibrium.

compound and its use facilitated the development of transfer and handling techniques, which require that air and moisture be excluded from the material at all stages.

The 20-percent triethylaluminum solution in benzene, when ignited in an open dish, burned with a flame not noticeably more smoky than that of pure benzene. The 20-percent solution reacts explosively in contact with liquid water, alcohols, or nitrobenzene. The explosive reaction with nitrobenzene can be avoided if that compound is diluted sufficiently with benzene. Under these circumstances the reaction of the nitrobenzene with triethyl aluminum occurred entirely in the liquid phase without development of flame or evolution of smoke.

The boiling point of triethyl aluminum is given as  $186^{\circ}\text{C}$ , whereas benzene boils at  $80^{\circ}\text{C}$ , so that when a solution containing mostly benzene is burned in an open tray, practically all the vapor feeding the flame, at least initially, will be benzene. To explore the effect of triethylaluminum as an additive to fuels having more nearly its own volatility, a supply of pure triethyl-aluminum was obtained and volumetric aliquots of it added to appropriate volumes of the fuels, to prepare solutions of known concentration, usually 10 percent by volume of triethylaluminum. It was found convenient to transfer the alkylaluminum from its cylinder to a pyrex serum bottle with a teflon stopper. The bottle together with the transfer line connecting it to the cylinder were purged several times with dry nitrogen before transfer. Aliquots of the triethylaluminum were transferred from the bottle to measured quantities of the fuels contained in nitrogen-purged serum bottles, by means of a purged hypodermic syringe of 1 cc capacity. The solutions were transferred from the serum bottles to the fuel tray of the burner in nitrogen-purged hypodermic syringes. The solutions were ignited immediately after transfer to the fuel tray.

The smoke yields of solutions containing 10 percent triethylaluminum in n-decane and in m-xylene were measured. They were slightly lower than the smoke yields of the pure fuels. In each case, a white powder remained in the fuel tray after the test. The weight of this residue was consistently the

calculated weight of aluminum oxide equivalent to the aluminum contained as additive in the fuel sample to within about 10 percent.

It would appear, therefore, that the triethylaluminum reacted with oxygen within the fuel tray in these experiments, instead of in the flame. Further evidence of this course of events was provided by a comparison of burning times, that of the solution with additive being only about two thirds as long as for the pure fuels. This could be due to accelerated evaporation of the fuel in the tray by energy released in oxidation of aluminum there.

More volatile organometallic compounds, containing magnesium, boron, or aluminum, and, perhaps, of slightly less pyrophoric nature than triethylaluminum might be more successful as additives to increase smoke production.

#### THE EFFECT OF SOLID DEHYDROGENATION CATALYSTS ON SMOKE YIELD

A series of experiments were performed in which solid catalysts were placed in the fuel tray of the apparatus for measurement of smoke yield, the fuel filling the interstices between the catalyst grains. The advantage expected of this arrangement was that the catalyst, together with the fuel would be heated by the transfer of energy from the flame, and that the fuel vapor, in passing the heated catalyst, would undergo some dehydrogenation with a consequent increase in its smoke yield.

Most of the solid catalysts tested were industrial dehydrogenation or oxidation catalysts manufactured by Harshaw Chemical Co., but simple mixtures of phosphorous pentoxide, of sodium azide, and of sodium amide with diatomaceous earth were also tested. Four of the Harshaw catalysts were intended for fluidized-bed application, so they were in the form of a free-flowing powder having median particle size of about 60 microns. This was a convenient grain size for our purpose, so the remaining catalysts, which were in the form of small cylindrical tablets, were ground and sieved to a size distribution approximating that of the powdered catalysts.

Three materials (glass microspheres, silicon carbide, and diatomaceous earth), thought to possess no special chemical catalytic activity, were tested to indicate whether the mere presence of granular material in the fuel tray would change the smoke yield due to physical effects such as a change in the schedule of heat transfer to the fuel, for example.

The glass microspheres were, fortuitously, of nearly the same particle size as the fluidized-bed catalysts, and the silicon carbide was ground and sieved to this size. The diatomaceous earth, however, was in its natural submicroscopic particulate form. One gram of catalyst powder (weighed to within 0.05 gram) was placed in the fuel tray for each experiment. The fuel was added immediately before ignition. Results are given in Table 7.

From the results given for the last three materials listed in Table 7, it would be inferred that benzene, burning over granular material having no special chemical catalytic activity, would have a smoke yield greater by about 5 percent than benzene burning alone. On the basis of this assumption, Harshaw catalyst Al-140iP Alumina Catalyst, and phosphorous pentoxide on diatomaceous earth both show a catalytic effect on smoke yield. Both of these catalysts are acidic. Sodium amide on diatomaceous earth, a strongly basic catalyst, also shows some activity. Other catalysts listed have negligible effect on the smoke yield except for Harshaw catalysts Fe-0303P Iron Catalyst, and Mn-0201-T Manganese Catalyst which appear to operate on n-hexane, but not on benzene.



Table 7

## EFFECT ON SMOKE YIELD OF COMBUSTION OVER SOLID CATALYSTS

Solid Catalyst Description	Fuel Burned On Catalyst	Smoke Yield	Burning Time (Sec)	Ratio of Effects With Solid Catalyst To Those With Fuel Alone	
				Smoke Yield	Burning Time
<b>Al-1401 P, Alumina Catalyst*</b> A microspheroidal high-activity alumina powder containing 97% $Al_2O_3$ specifically designed for fluid bed operations. Size: 0-20 $\mu$ 6% ABD 60 lb/ft <sup>3</sup> 20-40 $\mu$ 29% PV 0.49-.51 cc/g 40-80 $\mu$ 41% SA 180-200 m <sup>2</sup> /g +80 $\mu$ 24%	benzene m-xylene n-hexane	0.170 0.258 0.037	104 77 88	1.18 1.21 1.19	1.30 0.64 1.04
<b>Cr-1404 P, Chrome Alumina Catalyst*</b> A microspheroidal hydrodearomatization catalyst for fluid bed use. This powder contains 19% $Cr_2O_3$ , supported on high-activity alumina. ABD 58 lb/ft <sup>3</sup> 0-20 $\mu$ 1% SA 80-100 m <sup>2</sup> /g 20-40 $\mu$ 19% PV 0.59 cc/g 40-80 $\mu$ 34% +60 $\mu$ 46%	benzene n-hexane	0.151 0.029	34 94	1.05 0.93	1.17 1.11
<b>Fe-0303 P, Iron Catalyst*</b> A fluid bed microspheroidal hydrodearomatization catalyst containing 20% $Fe_2O_3$ mounted on high-activity alumina. ABD 68 lb/ft <sup>3</sup> SA 105 m <sup>2</sup> /g PV 0.49 cc/g	benzene n-hexane	0.151 0.037	104 53	0.92 1.29	1.30 1.09
<b>Mn-0201 T 1/8", Manganese Catalyst*</b> A black tableted oxidation catalyst containing 19% manganese dioxide mounted on activated alumina. ABD 70 lb/ft <sup>3</sup> SA 69 m <sup>2</sup> /g Strength 35 lb PV 0.23 cc/g	benzene n-hexane	0.146 0.038	84 86	1.01 1.24	1.05 1.91
<b>Mo-1101 P, Molybdena Alumina Catalyst*</b> Used for fluid bed hydroforming and dehydrogenation. A gray microspheroidal powder containing 11% $MoO_3$ mounted on high-activity alumina. ABD 68 lb/ft <sup>3</sup>	benzene n-hexane	0.133 0.022	82 88	0.92 0.72	1.22 1.04
<b>Ni-1601 T 1/8", Nickel Catalyst*</b> A decomposition catalyst containing 3 to 4% each nickel oxide, cobalt oxide and iron oxide mounted on activated alumina. ABD 62 lb/ft <sup>3</sup> SA 78 m <sup>2</sup> /g Strength 16 lb PV 0.28 cc/g	benzene n-hexane	0.146 0.031	98 91	1.01 0.99	1.22 1.07
<b>V-0601 T 1/8", Vanadia Catalyst*</b> Used for oxidation. Orange tablets containing 10% $V_2O_5$ mounted on high activity alumina. ABD 60 lb/ft <sup>3</sup> SA 115 m <sup>2</sup> /g Strength 26 lb PV 0.2 cc/g	benzene n-hexane	0.150 0.027	116 101	1.04 0.86	1.45 1.19

NOTE: Asterisked catalysts are manufactured by Harshaw Chemical Co. The descriptions are those given by them.

ABD - apparent bulk density, packed.

PV - pore volume.

SA - surface area.

Table 7 (cont)

Solid Catalyst Description	Fuel Burned On Catalyst	Smoke Yield	Burning Time (Sec)	Ratio of Effects With Solid Catalyst To those With Fuel Alone	
				Smoke Yield	Burning Time
Phosphorus Pentoxide - diatomaceous earth 1:3 by weight	benzene	0.170	89	1.18	1.11
	m-xylene	0.221	119	1.04	0.99
	n-decane	0.038	158	1.31	0.94
Sodium Azide - diatomaceous earth 1:3 by weight	benzene	0.133	121	0.92	1.51
	m-xylene	0.190	119	0.89	0.99
	n-decane	0.056	122	1.82	1.44
Sodium Amide - diatomaceous earth 1:3 by weight	benzene	0.164	83	1.14	1.15
	n-decane	0.045	155	1.54	0.92
Clay microspheres	benzene	0.154	71	1.07	0.89
Silicon carbide	benzene	0.157	63	1.09	0.79
Diatomaceous earth	benzene	0.148	126	1.03	1.57

## Section 7

## CONCLUSIONS AND RECOMMENDATIONS

A wide variation (about a factor of fifteen in the smoke yield) was found in the tendency of pure hydrocarbons to produce smoke when burned as fuels in air. Pure liquid hydrocarbons were tested that had up to approximately 2.4 times the smoke yield of benzene. The compounds of highest smoke yield appear to be of doubtful long-term stability in storage, so that the isomers of xylene, which produced about 1.5 times as much smoke per unit weight of fuel as benzene, appear to be an optimum practical choice of fuel.

Additives that were effective in increasing smoke yield produced percentage increases that were in an inverse relation to the intrinsic yields of the fuels to which they were added. Thus, while several fold increases in smoke yield were obtained in some cases for the normal paraffins which are poor smoke producers, no fuel additive was found to be capable of producing more than about 25-percent increase in the smoke yield of m-xylene.

Replacement of hydrogen in the hydrocarbon molecule, in particular by groups tending to withdraw electrons from the hydrocarbon radical to which they are attached, i.e., by electrophilic substituents, was found to be generally more effective in increasing smoke yield than the presence of additives in solution. The effectiveness of electrophilic substituents in increasing the smoke yields of hydrocarbons to which they are attached is consistent with the observation that the smoke yields of pure hydrocarbons measured in the present investigation correlate well with the strength of the hydrocarbons as carbon acids. The substitution of an electrophilic group for hydrogen in the hydrocarbon would be expected to withdraw electrons from the hydrocarbon, and thus increase its strength as a carbon acid.

The diminished effect of additives on hydrocarbons of higher intrinsic smoke yield is understandable if it is assumed that the effectiveness of the additives depends on their ability to further the acid dissociation of the fuel.

If it is assumed that a given additive produces the same percentage increase in the acid dissociation of two hydrocarbons of different intrinsic strength as carbon acids, the apparent acid dissociation constant of both hydrocarbons, with the additive, would be increased over their respective acid constants as pure hydrocarbons by the same factor. If the smoke yields are proportional to the logarithms of the acid constants as indicated by the correlation shown in Fig. 3, an increase in the acid constants of two hydrocarbons by a common factor would result in increases in the smoke yields by a common increment. The addition of the same increment to two different values of smoke yield, will not result in the same percentage increase in the two cases. The percentage increases in smoke yield will, instead, be in inverse proportion to the original yields.

Thus, for example, the fractional increase of the smoke yield of ethynylbenzene due to the presence of an additive would be about 0.085 as great as that of n-decane, and the increase in yield for m-xylene would be 0.66 that of benzene for the same additive if that additive produced the same fractional increase in the acid dissociation of each of these fuels. In the results given in Tables 3 and 4, the diminished fractional increase of smoke yield of fuels of higher intrinsic yields, due to the effect of a given additive, can be accounted for, in some cases, on the basis of the foregoing argument. In general, however, the fuels of high intrinsic yield show somewhat lower increases than this, relative to those of the low-yield hydrocarbons. It must therefore be assumed that the effect of the additives on the constants of the stronger carbon acids, in these instances, is somewhat less than its effect on the weaker carbon acids, or that other influences are active.

None of the smoke yields of fuel-additive mixtures or of substituted hydrocarbons, that were measured in the present investigation, fell more than a few percent higher than the maximum yield measured for pure hydrocarbons, namely, that of ethynylbenzene,  $C_6H_5C \equiv CH$ . This compound is one of the stronger carbon acids of those liquid hydrocarbons for which acid strength measurements have been made. Its smoke yield, given in Table 1, is 0.342. If the effectiveness of additives or electrophilic substitution in increasing smoke yield is principally due to the increased acid dissociation of the hydrocarbon that is

thus induced, and if this effect diminishes in the manner discussed above for hydrocarbons of high yield, it would appear that this means of increasing smoke yield is effective only up to a maximum of about 35 percent recovery of fuel carbon, in the particular apparatus employed to measure smoke yield in this investigation. Yields beyond this level presumably are barred by some feature of the smoke-making mechanism not appreciably influenced in any of the experiments in the present program.

It may be significant that the highest recovery for any of the processes used in the carbon black industry is also in the range of 30 to 40 percent (Ref. 9), although comparison of smoke yields measured under different conditions in different combustion systems is inherently uncertain.

Basic understanding is needed of the nature of the obstacles in the smoke production mechanism that stand in the way of obtaining 35 to 100 percent of the carbon in the fuel as smoke. Some insight to the problem may result from comparison of the conditions in the condensed and gaseous phases under which high yields of carbon are obtained in pyrolysis of hydrocarbons and their derivatives.

Differential thermal analysis\* of aromatic compounds conducted as a means of investigating the mechanism of their pyrolysis in the liquid or solid state, has shown (Ref. 10) a wide variation in the capacity of various compounds to deposit carbon as a residue. In these experiments, conducted at Union Carbide Corp., the sample and an inert reference material were heated together in an argon atmosphere at a rate of 10°C per minute to 750°C. The amount of carbon residue remaining at the end of the experiments was measured, and volatile products were collected for analysis. Some of the compounds tested produced no

---

\* Differential thermal analysis is an analytical method in which the temperature of a sample of the material under study is compared with the temperature of an inert reference material (such as anhydrous aluminum oxide) as both are heated together. Temperature regions where heat is absorbed by the sample (indicating endothermic reactions) or evolved (exothermic reactions) can be identified by irregularities they produce in the otherwise smoothly continuous temperature rise in the slowly heated sample and reference.

measurable carbon residue. A majority of the compounds produced small but measurable deposits containing of the order of 5 percent of the carbon contained in the fuel. About 25 percent of the compounds tested produced deposits of carbon greater than 34 percent of that contained in the fuel. In some of these cases, as much as 85 percent of the carbon in the fuel was deposited in the residue. The proclivity of these compounds toward large carbon residues had no apparent correlation with their volatility or other properties.

One of the simpler of the aromatic compounds tested, 2-nitrofluorene, produced 67.4 percent carbon residue. Its thermogram showed, in addition to the usual endotherm at the melting point ( $157^{\circ}\text{C}$ ), a single exotherm at  $303^{\circ}\text{C}$ . While it is not surely known that the carbon residue was deposited at the relatively low temperature of the exotherm, it was certainly deposited at temperatures less than  $750^{\circ}\text{C}$ , because this was the highest temperature to which the sample was heated. By way of contrast, when a hydrocarbon vapor diluted with an inert gas is heated, high yields of black carbonaceous smoke have not been reported at temperatures below about 900 to  $1000^{\circ}\text{C}$ , whatever the structure of the hydrocarbon.

It would appear, from these observations, that the capacity of organic compounds in the solid or liquid state to decompose in pyrolysis at low temperatures to deposit high yields of carbon is a fairly special and not very obvious function of the molecular structure of the compound. In the gaseous state, apparently, decomposition of organic compounds to form carbonaceous smoke can occur only at higher temperatures, regardless of the structure of the compound. This comparison, together with the remark of Palmer and Cullis (Ref. 6 P. 280) that "in contrast to the variety of surface carbons which may be formed (in pyrolysis), essentially one type of carbon is formed exclusively from the vapor phase" would suggest that an overriding limitation, peculiar to deposition of carbon in the vapor phase, determines the temperature required and the form of the deposit. This limitation must lie somewhere in the process of nucleation (or formation) of the carbon particles, since this is the only feature unique to deposition of carbon in the gas phase.

If it were found that the mechanism of nucleation was such that it could operate efficiently only at high temperature (1000°C or higher), this by itself might account for the limitation of smoke yields in combustion processes to a maximum of about 35 percent. The calculated equilibrium composition of the combustion products of benzene at 1300°K (1027°C)\* contains 34.3 percent of the carbon in the form of the unoxidized element. The fraction of carbon in elemental form at equilibrium rapidly diminishes as the equilibrium temperature is raised. Thus, if the combustion process operated not too far from equilibrium, and if efficient nucleation could occur only at temperatures of about 1000°C or greater, the fraction of total carbon that could be present in elemental form (as smoke) would be about 35 percent or less.

Further chemical investigation intended to improve the performance of carbon smoke generators would therefore need to seek an understanding of the mechanism of the formation of carbon smoke. This goal is of great interest and technological usefulness, however the investigation must be quite basic in nature, and possibly long-term as well.

In the immediate term, it is recommended that an investigation be conducted of the extent to which the performance of a full-scale prototype smoke generator, employing a hydrocarbon fuel with air as oxidizer, can be improved by optimizing the mode of mixing and degree of turbulence of the streams of fuel vapor and air, for greatest production of smoke. Experience in the carbon black industry has shown these physical factors to be important to the yield of carbon black obtained with a given fuel, and much of the work of their research and engineering divisions is reported (Ref. 9 p. 45) to be centered on the design and development of burners for best control of these factors.

---

\* The benzene is assumed to react with just sufficient oxygen (as air) that the energy released is sufficient to heat the products, at equilibrium, to 1300°K. The calculated fraction of carbon present, as the element, at equilibrium at 1300°K for hydrocarbons in general will not differ greatly from that calculated for benzene.

## Section 8

## REFERENCES

1. Goodale, T. C., M. B. Hawkins, and A. B. Willoughby, Feasibility of Active Countermeasures for Thermal Radiation Effects of Nuclear Weapons, URS 617-4, United Research Services, Burlingame, Calif., July 1963 (AD-412 733)
2. M. Staackmann, et al., Final Results of Smoke Screen System Development, Final Report URS 643-9, URS Corporation, June 1966
3. Donald J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, Inc., 1965
4. A. I. Shatenshtein, Isotopic Exchange and Replacement of Hydrogen in Organic Compounds, Consultants Bureau, New York, 1962
5. A. Morton, "Behaviour of Organoalkali Compounds," Chem. Rev., 35, (1944) pp.1-49
6. H. B. Palmer and C. F. Cullis, Chemistry and Physics of Carbon, A Series of Advances, Vol. I Edited by Phillip L. Walker Jr., Marcel Dekker, Inc., New York, 1965
7. E. Ott and F. Ohse, Ber., 54 B 179-86 (1921) also; Chem. Abstr., 15 2069 (1921)
8. Taylor and Rinkenbach, Bureau of Mines, R. I. 2513 (1923)
9. The Interscience Encyclopedia, Inc., Encyclopedia of Chemical Technology, Vol. 3, 1949, p. 46
10. Union Carbide Corporation, Advanced Materials Laboratory, Improved Graphite Materials for High-Temperature Aerospace Use, ML-TDR-64-125, Vol I



UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing notation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) URS Systems Corporation 181 <sup>st</sup> Trousdale Drive Burlingame, California 94010		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE  Improvement of the Performance of Carbon Smoke Generators by the Choice of Fuels and Fuel Additives			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report			
5. AUTHOR(S) (First name, middle initial, last name)  Goodale, Thomas			
6. REPORT DATE July 8, 1968		7a. TOTAL NO. OF PAGES 37	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. N0022867C2089		9a. ORIGINATOR'S REPORT NUMBER(S) URS 678-4	
8b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT  This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Civil Defense Washington, D.C. 20310	
13. ABSTRACT An experimental investigation was conducted of the improvement in performance of a simple carbon smoke generator, employing a hydrocarbon fuel and air as oxidizer, that could be obtained by appropriate choice of fuels and of various additives to the fuels. The smoke yield of pure hydrocarbons, defined as the weight of carbonaceous smoke recovered per unit weight of carbon in the fuel burned, varied widely among the hydrocarbons tested, the extremes differing by a factor of 15. The smoke yields of most of the hydrocarbons and hydrocarbon derivatives correlated well with their strength as carbon acids, i.e., their tendency to dissociate to form carbanions. Strong Lewis-acids and bases and halogen - containing flame inhibitors, as additives, increased the smoke yield of hydrocarbons. The fractional increase in smoke yield thus produced was in inverse relation to the intrinsic smoke yield of the hydrocarbon burned. An argument is given to show that the diminished fractional increase in the smoke yields of hydrocarbons of high intrinsic yield of smoke may be due in large part to the form of the correlation found between the smoke yield of hydrocarbons and their strength as carbon acids. Oxygen-enrichment of the air supply to the burner was found to cause the smoke yield of benzene to approximately double in value. The smoke yield of cyclopentadiene increased 50 percent when supplied with oxygen-enriched air, but the effect was modest or negligible in the case of other hydrocarbons tested.			

